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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

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Applicant UNIVERSITY OF WATERLOO ET AL		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>3</u> sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p style="margin-left: 20px;">a. <input checked="" type="checkbox"/> (<i>sent to the applicant and to the International Bureau</i>) a total of <u>20</u> sheets, as follows:</p> <p style="margin-left: 40px;"><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. 1 and the Supplemental Box.</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> (<i>sent to the International Bureau only</i>) a total of (indicate type and number of electronic carrier(s)) _____, containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand 06 June 2005 (06-06-2005)	Date of completion of this report 08 March 2006 (08-03-2006)	
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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/CA2004/002111

Box No. I Basis of the report

1. With regard to the **language**, this report is based on:
 - ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of:
 - ☐ international search (Rules 12.3(a) and 23.1(b))
 - ☐ publication of the international application (Rule 12.4(a))
 - ☐ international preliminary examination (Rules 55.2(a) and/or 55.3(a))
2. With regard to the **elements** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:
 - ☐ the international application as originally filed/furnished
 - ☒ the description:
 - ☒ pages 2, 4, 7, 9 - 14, 17 - 53 as originally filed/furnished
 - ☒ pages* 1, 1a, 3, 5, 6, 6a, 8, 8a, 15, 15a, 16, & 16a received by this Authority on 06-06-2005
 - ☐ pages* _____ received by this Authority on _____
 - ☒ the claims:
 - ☐ pages _____ as originally filed/furnished
 - ☐ pages* _____ as amended (together with any statement) under Article 19
 - ☒ pages* 54 - 61 (claims 1 - 47) received by this Authority on 22-02-2006
 - ☐ pages* _____ received by this Authority on _____
 - ☐ the drawings:
 - ☐ pages _____ as originally filed/furnished
 - ☐ pages* _____ received by this Authority on _____
 - ☐ pages* _____ received by this Authority on _____
 - ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.
3. ☐ The amendments have resulted in the cancellation of:
 - ☐ the description, pages _____
 - ☐ the claims, Nos. _____
 - ☐ the drawings, sheets/figs _____
 - ☐ the sequence listing *(specify)*: _____
 - ☐ any table(s) related to sequence listing *(specify)*: _____
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
 - ☐ the description, pages _____
 - ☐ the claims, Nos. _____
 - ☐ the drawings, sheets/figs _____
 - ☐ the sequence listing *(specify)*: _____
 - ☐ any table(s) related to sequence listing *(specify)*: _____

* If item 4 applies, some or all of those sheets may be marked "superseded."

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/CA2004/002111

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	<u>1 - 47</u>	YES
	Claims	<u>None</u>	NO
Inventive step (IS)	Claims	<u>1 - 47</u>	YES
	Claims	<u>None</u>	NO
Industrial applicability (IA)	Claims	<u>1 - 47</u>	YES
	Claims	<u>None</u>	NO

2. Citations and explanations (Rule 70.7)

Novelty:

Claims 1 - 47 are directed to novel subject matter and thus comply with Article 33(2) PCT.

Present claims 1 - 16 and 41 - 43 are directed to the use of catalytic composites as a **random packing material and catalyst** in a catalytic distillation apparatus. Subsequent claims 17 - 40 and 44 - 47 are directed to dimerization, oligomerization, and/or hydrogenation processes which employ the aforementioned catalytic composites in a catalytic distillation apparatus.

The closest prior art, WO 02/092216, is directed to catalytic composites having the same void fraction and surface area as the composites of the instant claims, however, the composites of WO 02/092216 comprise a regular structure and are used as a **unitary monolithic packing material and catalyst** in the catalytic distillation apparatus. The prior art thus differs from the claims of the instant application.

Inventive Step:

Claims 1 - 47 are directed to inventive subject matter and thus comply with Article 33(3) PCT.

The prior art does not disclose or suggest the use of catalyst composites as a random packing material and catalyst in a catalytic distillation apparatus, or dimerization, oligomerization, and/or hydrogenation processes which employ the aforementioned catalysis composites in a catalytic distillation apparatus.

Industrial applicability:

Claims 1 - 47 are considered to have industrial applicability and thus comply with Article 33(4) PCT.

COMPOSITE CATALYST FOR THE SELECTIVE OLIGOMERIZATION OF LOWER ALKENES AND THE PRODUCTION OF HIGH OCTANE PRODUCTS

FIELD OF THE INVENTION

This invention relates to the oligomerization of lower
5 alkenes and mixtures of alkenes by catalytic distillation.
More specifically, the invention relates to a catalytic
composite as a catalyst and packing media in a catalytic
distillation column for the selective oligomerization of
lower alkenes. In addition, the invention also relates to
10 the hydrogenation of alkenes or of the products from the
selective oligomerization to produce high octane products.

BACKGROUND OF THE INVENTION

Catalytic distillation (CD) combines catalytic reaction and
separation in a single distillation unit. This idea was
15 first implemented early in the 1920s for the production of
esters (Backhaus, US Patent No. 1,400,849) and has been
applied to a number of chemical processes based on
homogeneous catalysts. The advantages of combining reaction
and separation were not fully appreciated until 1980, when
20 Smith patented a new catalytic distillation technology using
heterogeneous catalysts (Smith, US Patent No. 4,232,177).

Conventional chemical processes that utilise a distillation
process (non-catalytic) mainly consist of two separate unit
operations. These include a unit hosting chemical reactions
25 and another unit for separating the different components
from the resulting reaction mixture. Under such
circumstances, it is difficult to recycle the heat produced
by the chemical reaction, and cooling is often needed to
control the temperature in the reaction zone, thus resulting
30 in ineffective energy utilization in the process. In

addition, the productivity of a preferred compound is often

sufficient catalyst is placed into the column without significantly increasing the pressure drop. It was not until 1980 that Smith (US Patent No. 4,232,177) patented a method of suspending catalyst pellets inside a distillation column using fibreglass containment bags, which are known as Texas teabags. Use of these bags permits the use of heterogeneous catalysts without giving rise to large increases in pressure drop. In contrast to homogeneous catalytic distillation, heterogeneous catalytic distillation is preferentially termed catalytic distillation (CD).

In the CD process, the solid catalyst has to be packed in a suitable manner inside the distillation column so as to maximize contact between vapour and liquid phases, but to minimize column flooding. Indeed, various methods have been reported for supporting or containing catalysts [Crossland et al., US Patent 5,431,890; Hearn, US Patent 5,266,546; Shelden, US patent 5,417,938]. It should be noted that with all these methods, the catalyst is enclosed inside a device which can increase the mass transfer resistance of the liquid and gas phases in the column.

Since a catalytic distillation process combines heterogeneous reaction and separation in a single distillation column, the following advantages can often be obtained over conventional fixed bed reactors:

- i) The capital and production costs are reduced because two operations are combined in a single unit.
- ii) The energy consumption can be minimized as the heat of the reaction is used for the in-situ vaporization of the reactants.
- iii) The conversion of the reactant can be enhanced through internal recycling.

ii) The catalyst should be heterogeneous and stable thermally as well as chemically and physically to retain its structural integrity for maintenance of a long lifetime.

iii) The reaction should be exothermic and in

5 situations where the reaction is equilibrium limited, the CD process presented the option to shift that equilibrium more to the right to achieve higher conversion and higher productivity much more efficiently.

One chemical reaction that satisfies these requirements is
10 the oligomerization of lower alkenes (alkene molecules having from 2 to 6 carbon atoms). Alkylation and oligomerization of lower alkenes was first disclosed by Huss and Kennedy (US Patent No. 4,935,577) and Smith et al. (US Patent No. 5,003,124). The oligomerization of lower alkenes
15 is an important industrial reaction and represents a route to the production of intermediates used for the production of motor fuels, plasticizers, pharmaceuticals, dyes, resins, detergents, lubricants and additives (O'Connor and Kojima, 1990). With respect to butene oligomerization, the less
20 branched dimer products, octenes, are particularly useful in the manufacture of plasticizers. If heavily branched, the mixture can be used as a gasoline blender.

Historically, the exploitation of all of the C₄ fractions obtained as by-product from hydrocarbon fluid catalytic
25 cracking and steam cracking to produce high value products (high octane value product) has been lacking. Butadiene, a component of the by-product is useful for rubber production and is extracted from the by-product, leaving the remaining C₄ fractions as a mixture referred to as Raffinate I. The
30 isobutene that is contained in Raffinate I was used as a source for production of methyl tert-butyl ether (MTBE). The remaining components of the C₄ fractions after the removal of

06 JUNE 2005 06.06.05

isobutene, consisting mainly of linear C₄ hydrocarbon (butenes), was mainly used as a gasoline blender, albeit a poor one. In certain cases, this product was simply disposed of by flaring. In Raffinate II, n-butene is present at an average content from 70% to 80% and in some cases can be in the ninety percentage ranges. Using this resource, smaller oligomers, particularly C₈ and C₁₂, are being produced by current catalytic oligomerization processes.

A variety of butene oligomerization processes have been proposed (Keim et al, J. Mol. Catal., 6, 79, 1979; Mathys et al, US Patent No. 4,476,341; and Beltrame et al., Appl. Catal., A: general, 100, 39-48, 1994) based on homogeneous and heterogeneous reactions. These processes are exclusively focused on the catalyst selection and process optimization so that a high oligomerization rate with a high selectivity to desired products, mainly short and less branched oligomers, can be obtained.

The use of catalytic distillation to enhance the oligomerization of alkenes was first disclosed in US Patent No. 5,003,124 to Smith in 1991. This process utilized an acidic ion exchange resin placed inside a fibre glass bag.

Further research has been carried out in the field of alkene oligomerization, but in most cases, the oligomerization catalyst is contained within a second structure such as a cloth or mesh bag, and the reactants have to pass through this structure to access the catalyst. Likewise, the products have to pass through the structure to be removed away from the catalyst. In one such example, Podrebarac ("The Dimerization of 1-Butene Using Catalytic Distillation", M.A. Sc. Thesis, University of Waterloo, 1992) studied butene dimerization in a CD column using a

nickel exchanged zeolite catalyst, where the zeolite was placed directly in fibreglass bags. The zeolite catalyst in this case was quickly deactivated by the production of undesirable long chain oligomers, which oligomers blocked

hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body; and

b) from 0.01 to 10% by weight of a catalytically active species, based on the weight of the catalyst, which is deposited on the support structure.

In another aspect, the present invention provides a catalytic composite for use as a hydrogenation catalyst in a catalytic distillation apparatus, the catalytic composite comprising:

a) a support structure, made of an inorganic oxide, having a void fraction ranging from 0.30 to 0.95 and a crush strength of from 2.4 to 9.9 kg per structure unit, the support structure having a shape selected from a ring, a hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body; and

b) from 0.01 to 10% by weight of palladium, platinum or rhodium, based on the weight of the catalytic composite, which is deposited on the support structure. In one embodiment, the inorganic oxide forming the support structure of the hydrogenation catalyst is an α -alumina, for example an α -alumina having a surface area of from 0.1 to 1.0 m²/g.

In still another aspect, the present invention provides a process for the selective oligomerization of a lower alkene to a C₆-C₁₈ alkene, which process comprises contacting the lower alkene with a catalytic composite as described herein, under catalytic distillation conditions.

In still another aspect, the present invention provides a process for the hydrogenation of an alkene to an alkane, which process comprises contacting the alkene with a catalytic composite as described herein, and hydrogen, under
5 catalytic distillation conditions.

properties comprising of both components to constitute or form the catalytic composite.

Various catalytically active species can be deposited on the support structures described above to give the catalytic composite. Examples of active species include metals and metal ions from Groups VI, VII and VIII. These metals or metal ions can be loaded from corresponding metal salts or metal complexes. Of these metals and metal ions, nickel ions loaded from nickel salts, which are especially effective for the oligomerization of lower alkenes, are preferred as the active species for oligomerization. Examples of metal salts include metal sulphate, metal phosphate, metal oxalate and metal acetate. More preferably, the nickel ions loaded from aqueous solutions of nickel sulphate, or aqueous solutions of nickel chloride and ammonium sulphate are used as the active catalytic species. Metals used as the catalytic species for oligomerization are also preferably in the +1 or +2 oxidation state. As the oligomerization is acid catalysed, acid and acidic salts can be deposited on the support and used as catalyst. In addition, the oligomerization catalysts comprising nickel ions can be further enhanced through exposure to solutions of sulphate salts such as ammonium sulphate, phosphate salts such as ammonium phosphate and acids such as sulphuric acid, phosphoric acid or toluenesulfuric acid. Such solutions are herein referred to as catalyst enhancers.

The catalytically active species are not necessarily metallic, as certain salts, such as ammonium sulphate, can be used. For example, ammonium sulphate is a suitable catalytically active species for the dimerization of isobutene in the presence of hydrogen.

Metal loaded from metal complexes of palladium, platinum, rhodium and nickel are effective for hydrogenation of alkenes, including hydrogenation of octenes and methyl

substituted pentenes produced by the oligomerization of butenes by the nickel catalyst described herein. Metal complexes can contain ligands comprising, for example, one or more carbon, hydrogen, oxygen, nitrogen and phosphorus atoms. Metal salts can also be used as catalytic species in the hydrogenation process if the metal ions derived from the salts can be reduced to give metal species that are active.

The amount of catalyst species on the support structure is dependent on the concentration of metal salt or the metal complex in solution, and to a lesser extent on the length of the exposure period of the support structure to the solution. The amount of catalytic species can be from 0.01 to 10% by weight, for example of from 0.05 to 10% or from 0.1 to 8% by weight.

A catalytic composite for use as an oligomerization catalyst can, for example, contain nickel in an amount of from 0.1 to 8% by weight, relative to the weight of the composite. Preferably, the amount of nickel is from 0.2 to 6.0% by weight, and more preferably, from 0.5% to 5% by weight.

A catalytic composite for use as a hydrogenation catalyst can, for example, contain palladium in an amount of from 0.05 to 8% by weight, relative to the weight of the composite. Preferably, the amount of palladium can be, for example, from 0.1 to 8%, from 0.2 to 6%, from 0.2 to 5%, from 0.5 to 5% or from 0.3 to 2% by weight.

Deposition of the metal ions on the support structure can be effected by methods known in the art. Examples of such methods include wet and dry impregnation methods, vaporization methods, absorption techniques, ion-exchange techniques, sol-gel techniques and vapour deposition

techniques. A description of such techniques is given in examples 1a and 1b.

Catalytic Distillation Packing

We claim:

1. A catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus, the catalytic composite comprising:

a) a support structure, made of a non zeolite inorganic oxide, having a void fraction ranging from 0.30 to 0.95 and a surface area of from 40 m²/g to 500 m²/g, the support structure having a shape selected from a ring, a hollow cylinder, a cross or multi partition ring or cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body; and

b) from 0.01 to 10% by weight of a catalytically active species comprising a group VIII metal, based on the weight of the catalytic composite, which is deposited on the support structure.

2. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to claim 1, wherein the void fraction is from 0.30 to 0.95 and the surface area is from 50 m²/g to 500 m²/g.

3. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to claim 1 or 2, wherein the inorganic oxide is selected from the group consisting of alumina, silica, titania, zirconia and mixtures thereof.

4. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to claim 1 or 2, wherein the inorganic oxide is γ -alumina.

22 FEBRUARY 2006 22-02.06

5. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to claim 1 or 2, wherein the inorganic oxide is α -alumina.

5 6. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to any one of claims 1 to 5, wherein the support structure is in the shape of a Raschig ring.

7. The catalytic composite for use as a random packing
10 material and catalyst in a catalytic distillation apparatus according to any one of claims 1 to 6, wherein the group VIII metal is nickel.

8. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus
15 according to any one of claims 1 to 7, wherein the group VIII metal is in the form of a metal salt or a metal complex.

9. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus
20 according to claim 8, wherein the metal salt is in an ionic state.

10. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to claim 8, wherein the metal salt is a
25 metal sulphate, a metal phosphate, a metal oxalate or a metal acetate.

11. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to any one of claims 1 to 6, wherein
30 the catalytically active species is nickel sulphate.

22 FEBRUARY 2006 22-02.06

12. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to any one of claims 1 to 6, wherein the catalytically active species is nickel chloride.

5 13. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to any one of claims 9 to 12, wherein the catalytically active species is in admixture with ammonium sulphate or ammonium phosphate.

10 14. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to any one of claims 1 to 6, wherein the catalytically active species comprises a group VIII metal and a ligand, wherein the ligand comprises one or
15 more atoms selected from the group consisting of carbon, hydrogen, oxygen, nitrogen and phosphorus.

15. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to claim 14, wherein the group VIII
20 metal is in the zero oxidation state.

16. The catalytic composite for use as a random packing material and catalyst in a catalytic distillation apparatus according to any one of claims 1 to 6, wherein the group VIII metal is palladium, platinum or rhodium.

25 17. A process for the selective dimerization of a lower alkene to a C₆-C₁₂ alkene, which process comprises contacting the lower alkene with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions.

22 FEBRUARY 2006 22-02.06

18. The process according to claim 17, wherein the lower alkene is selected from 1-butene, 2-butene and isobutene, and the C₆-C₁₂ alkene is selected from trimethylpentene, n-octene, dimethylhexene and methylheptene.

19. The process according to claim 17 or 18, wherein the catalytic composite is admixed with inert distillation packing.

20. The process according to claim 19, wherein the ratio of the catalytic composite to inert distillation packing is from 10:1 to 1:10.

21. The process according to claim 19, wherein the catalytic composite and inert distillation packing are used in separate zones of the catalytic distillation column.

22. The process according to claim 17, wherein the lower alkene is a C₄ alkene and the C₆ to C₁₂ alkene is predominantly a C₈ alkene.

23. The process according to claim 22, wherein the C₈ alkene is a trimethylpentene.

24. A process for the hydrogenation of an alkene to an alkane, which process comprises contacting the alkene with a catalytic composite as claimed in any one of claims 14 to 16, and hydrogen, under catalytic distillation conditions.

25. The process according to claim 24 wherein the alkene is selected from trimethylpentene, n-octene, dimethylhexene and methylheptene.

26. The process according to claim 24 or 25, wherein the catalytic composite is admixed with inert distillation packing.

27. The process according to claim 26, wherein the ratio of the catalytic composite to inert distillation packing is from 10:1 to 1:10.

5 28. The process according to claim 26 wherein the catalytic composite and inert distillation packing are used in separate zones of the catalytic distillation column.

29. The process according to any one of claims 24 to 28, wherein the alkene is trimethylpentene and the alkane is trimethylpentane.

10 30. A process for preparing high octane compounds, the process comprising:

15 a) contacting a C₂ to C₆ alkene with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions, to obtain a C₆ to C₁₈ alkene; and

b) contacting the C₆ to C₁₈ alkene from step a) with a catalytic composite as claimed in any one of claims 14 to 16, and hydrogen, under catalytic distillation conditions, to obtain a C₆ to C₁₈ alkane.

20 31. The process according to claim 30, wherein the process steps a) and b) are carried out in a single catalytic distillation column.

25 32. The process according to claim 30, wherein the process steps a) and b) are carried out in separate catalytic distillation columns.

33. The process according to claim 30 or 31, wherein the C₂ to C₆ alkene is a C₄ alkene and the C₆ to C₁₈ alkene is a C₈ alkene.

34. The process according to claim 33, wherein the C₈ alkene is trimethylpentene.

35. A process for preparing high octane compounds, the process comprising:

5 a) contacting isobutene with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions, to obtain trimethylpentene; and

b) contacting trimethylpentene with a hydrogenation catalyst, and hydrogen, under batch reaction
10 conditions or under hydrogenation reaction conditions to obtain trimethylpentane.

36. A process for the production of C₆-C₁₈ alkenes, which process comprises contacting a mixture of C₂-C₆ alkenes with a catalytic composite as claimed in any one of
15 claims 1 to 16, under catalytic distillation conditions.

37. A process according to claim 36, wherein each C₂-C₆ alkene in the mixture is oligomerized within different reactive zones found in a single catalytic distillation column.

20 38. A process according to claim 36, wherein each C₂-C₆ alkene is oligomerized within different reactive zones found in two or more linked catalytic distillation column.

39. A process according to any one of claims 36 to 38, wherein the mixture of C₂-C₆ alkenes comprises one or more
25 C₄ alkenes.

40. A process for the selective oligomerization of a lower alkene to a C₆-C₁₈ alkene, which process comprises contacting a mixture of C₂ to C₆ alkenes and C₁ to C₆

22 FEBRUARY 2006 22-02.06

alkanes with a catalytic composite as claimed in any one of claims 1 to 16, under catalytic distillation conditions.

41. A catalytic composite for use as a random packing hydrogenation catalyst in a catalytic distillation

5 apparatus, the catalytic composite comprising:

a) a support structure, made of an inorganic oxide and having a void fraction ranging from 0.30 to 0.95, the support structure having a shape selected from a ring, a hollow cylinder, a cross or multi partition ring or
10 cylinder with 2, 3, or 4 cell partitions, a saddle, a solid ring, a solid cylinder, a sphere, and a honeycomb body; and

b) from 0.01 to 10% by weight of palladium, platinum or rhodium, based on the weight of the catalytic composite, which is deposited on the support structure.

15 42. The catalytic composite for use as a random packing hydrogenation catalyst in a catalytic distillation apparatus according to claim 41, wherein the inorganic oxide is α -alumina.

20 43. The catalytic composite for use as a random packing hydrogenation catalyst in a catalytic distillation apparatus according to claim 42, wherein the α -alumina has a surface area of from 0.1 to 1.0 m²/g.

25 44. A process for the hydrogenation of butadiene, the process comprising contacting butadiene with a catalytic composite as claimed in any one of claims 41 to 43, and hydrogen, under catalytic distillation conditions.

45. A process for the selective hydrogenation of methylacetylene and propadiene in a C3 fraction to provide propylene, the process comprising contacting the C3

fraction with a catalytic composite as claimed in any one of claims 41 to 43, and hydrogen, under catalytic distillation conditions.

5 46. A process for the selective hydrogenation of allene and propyne in a fluid catalytic cracking (FCC) stream, the process comprising contacting the FCC stream with a catalytic composite as claimed in any one of claims 41 to 43, and hydrogen, under catalytic distillation conditions.

10 47. A process for the selective hydrogenation of butadiene in a raffinate I or a raffinate II stream to provide a butene, the process comprising contacting the raffinate I or the raffinate II stream with a catalytic composite as claimed in any one of claims 41 to 43, and
15 hydrogen, under catalytic distillation conditions.